

PATENT SPECIFICATION

(11) 1 372 368

1 372 368

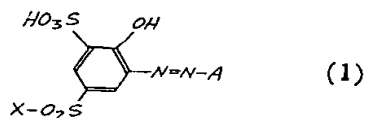
- (21) Application No. 46886/71 (22) Filed 8 Oct. 1971
 (31) Convention Application No. 2 049 664 (32) Filed 9 Oct. 1970 in (19)
 (33) Germany (DT)
 (44) Complete Specification published 30 Oct. 1974
 (51) International Classification C09B 62/74, 45/00
 (52) Index at acceptance
 C4P 8A1B 8A1E 8B1 8C3 8D2 8E



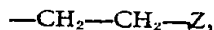
(54) METAL COMPLEX MONOAZO DYES AND PROCESS FOR THEIR MANUFACTURE

(71) We, FÄRBFWERKE HOECHST AKTIENGESELLSCHAFT, vormals Meister Lucius & Brüning, a body corporate organised according to the laws of Germany, of 6230 Frankfurt (Main) 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides water-soluble copper, chromium and cobalt complex compounds of monoazo dyes which, in the non-metallized form and in the form of the free acid, are of the general formula (1)



in which formula X represents a vinyl group or a group of the formula

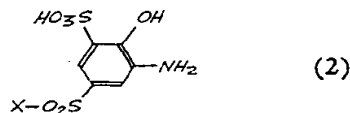


Z representing a hydroxyl group or an inorganic or organic radical that can be split off by an alkaline agent, and A represents a radical of a coupling component of the phenol, aniline, naphthol, or naphthylamine series, the hydroxy or amino group of which is *ortho* to the azo group, a radical of a coupling component of the 5-(hydroxy or amino)-pyrazole series, additionally substituted in the 1- and 3-positions, or a radical of a coupling component of the acetoacetic acid arylamide series, and any sulphonic acid group in the compound being in the free acid form or in the form of a sulphonate group.

The metal complex azo dyestuffs of the invention are either 1:1- or 1:2-metal complex compounds depending on whether the metal atom is bound to one dyestuff residue (as is the case with copper and chromium) or to two dyestuff residues (as is the case with chromium and cobalt).

The copper complex compounds are of particular importance, especially those compounds in which X represents a β -sulphatoethyl group.

This invention also provides a process for the manufacture of a metal complex compound of the invention, which process comprises diazotizing an amine of the general formula (2)



in which X is defined as above, coupling it with a coupling component of the general formula (3)



(3)

5 in which A is defined as above; and treating the monoazo dye of the general formula (1) thus obtained, with a copper, chromium or cobalt-yielding agent. 5

Suitable coupling components of the general formula (3) are, for example:

(i) an aniline or phenol, for example 1,3-diamino-benzene-4-sulphonic acid, 1,3-dihydroxy-benzene, 1,3-dihydroxy-4-methyl-benzene, 1,3-dihydroxy-benzene-4-sulphonic acid or 1,3-dihydroxy-benzene-4-carboxylic acid;

10 (ii) an acetoacetic acid arylamide, the aryl radical of which may be further substituted by, for example, a halogen atom and/or a methyl, methoxy or sulphonic acid group and/or a group of the formula 10



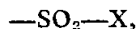
15 X being defined as above;

(iii) a pyrazole that contains in the 5-position a hydroxyl or amino group, in the 3-position a further substituent, for example a methyl, ethyl, carboxyl, carboxylic acid ester, or carboxylic acid amide group, and in the 1-position a further substituent, for example an unsubstituted or substituted phenyl group, possible substituents being, for example, a chlorine atom, methyl group, methoxy group, sulphonic acid group, and a group of the formula 20



25 X being defined as above; and

(iv) a hydroxy- or amino-naphthalene, which may be further substituted by, for example, one or more substituents selected from methyl, methoxy, amino, acylamino, hydroxy, groups of the formula 25



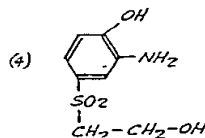
X being defined as above, and especially sulphonic acid groups.

30 As examples of the inorganic or organic radical Z that can be split off by an alkaline agent there may be mentioned: a halogen atom, for example a chlorine or bromine atom; an alkyl- or arylsulphonic acid ester group, for example a methylsulphonyloxy or *p*-toluenesulphonyloxy radical; an acyloxy group (preferably having up to 6, more preferably up to 4, carbon atoms), for example an acetoxy group or a 3-sulphobenzoyloxy group; a phenoxy group;

35 a dialkylamino group (preferably having up to 6, more preferably up to 4, carbon atoms in each alkyl moiety), for example a dimethylamino or diethylamino group; a thiosulphuric acid ester group; a phosphoric acid ester group; and, especially, a sulphuric acid ester group.

40 The term "alkaline agent" should be understood by those skilled in the art. It includes not only alkalis but also substances that have an alkaline action in water in water or that yield a substance having an alkaline action when heated. 40

An amine of the general formula (2) in which X represents a β -sulphatoethyl group ($-\text{CH}_2-\text{CH}_2-\text{O}-\text{SO}_3$) can be prepared by reacting the amine of formula (4)



45 with a sulphonating agent, for example sulphur trioxide, chlorosulphonic acid or, preferably, sulphuric acid containing free sulphur trioxide (oleum). If oleum is used, the reaction may suitably be carried out at a temperature of from 100 to 45

200°C. The resulting compound is 2-amino-4-(β -sulphatoethylsulphonyl)-phenol-6-sulphonic acid, which may then be coupled with a compound of the general formula (3).

The β -sulphatoethyl group ($-\text{CH}_2-\text{CH}_2-\text{O}-\text{SO}_3$), formed as described above, may be converted into a β -hydroxyethyl group ($-\text{CH}_2-\text{CH}_2-\text{OH}$) or a vinyl group ($-\text{CH}=\text{CH}_2$), if desired, in order to form dyes wherein, in general formula (1), X represents a group other than a β -sulphatoethyl group. Furthermore, the vinyl group and the β -hydroxyethyl group may be converted by suitable addition reaction and by suitable esterification respectively, into further groups represented by X. These conversions (from the β -sulphatoethyl group and/or from the vinyl or β -hydroxyethyl group) may be effected on the amine of general formula (2) prior to diazotization and coupling, on the mono azo dye of general formula (1) prior to metallization, or on the metal complex compound itself. Four examples of how such conversions may be effected are detailed below:

(i) a β -sulphatoethyl group may be converted into a β -hydroxyethyl group by hydrolysis in an aqueous acidic solution of pH not greater than 2; if this reaction in a strongly acid solution is carried out on the metal complex compound, the complex may be destroyed and have to be reformed by raising the pH;

(ii) a β -sulphatoethyl group may be converted into a vinyl group by treatment with an alkali, for example sodium carbonate or sodium hydroxide;

(iii) a vinyl group may be converted into a β -thiosulphatoethyl group by reaction with a thiosulphate, for example sodium thiosulphate; and

(iv) a vinyl group may be converted into a β -(dialkylamino)-ethyl group by reaction with a dialkylamine, for example dimethylamine or diethylamine.

Methods for the metallization of *o,o'*-dihydroxy and *o*-hydroxy-*o'*-amino dyes have been described, for example, in Houben-Weyl, *Methoden der organischen Chemie*, 4th edition (1965), Vol. 10/3, page 434. Such methods may be used for the preparation of the metal complex compounds of the invention.

The isolation of the metal complex azo dyes of the invention may be effected by salting out, for example with sodium chloride or potassium chloride, or by spray drying of the reaction mixture.

The metal-containing monoazo dyes of the invention are very suitable for dyeing and printing leather and various fibrous materials, for example wool, silk, synthetic polyamide fibrous materials, and especially natural or regenerated cellulose fibrous materials (for example cotton and linen). They may preferably be used according to the dyeing and printing processes generally used in industry, such as have been described, for example, in *Melliand Textilberichte* 1959, 539 and 1965, 286. The metal complex monoazo dyes of the invention yield for example on cellulose fibrous materials in the presence of alkaline agents, intense dyeings and prints having good fastness properties to light and to wet processing.

The metal complex azo dyes of the invention are substantially superior to the comparable dyes described in German Patent Specifications Nos. 1,126,547 and 1,103,886 with respect to the colour build-up according to dyeing and printing processes.

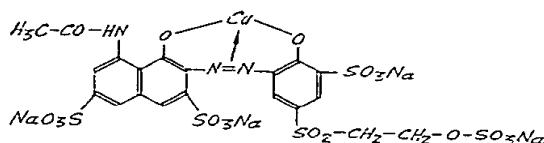
The following Examples illustrate the invention, the parts and percentages being by weight, unless stated otherwise. The relationship between parts by volume and parts by weight is as that between millilitres and grams.

Example 1.

217 parts of 2-amino-4-(β -hydroxyethylsulphonyl)-phenol were introduced, without cooling, into 500 parts of 100% sulphuric acid (monohydrate) while stirring, and heated at 120°C. After complete solution, 260 parts of sulphuric acid which contained 65% of free sulphur trioxide (i.e. 65% oleum) were added dropwise at that temperature over 2 hours. Stirring of this mixture was continued for another 1 to 2 hours at 120°C, and then added to 3000 parts of ice after cooling and while stirring. After the addition of 200 parts by volume of 5 N sodium nitrite solution, which was led in under the surface at 0° to +5°C while stirring, stirring was continued for 15 to 30 minutes and any excess of nitrite that may have been present was decomposed by the addition of 2 to 3 parts of amidosulphonic acid.

By adding 600 parts of calcium carbonate in portions, the pH was reduced to 2 to 3, and by simultaneously adding a further 2000 parts of ice, the temperature was maintained below +10°C. Then, a neutral solution of 361 parts of 1-hydroxy-8-acetyl-amino-naphthalene-3,6-disulphonic acid in 1500 parts of water was added. When a further 100 parts of calcium carbonate and finally 50 parts of sodium carbonate

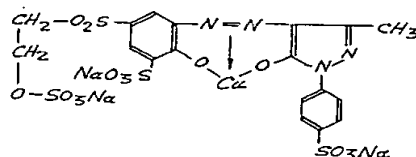
had been added, the pH was adjusted to 6 to 6.5. After coupling had been completed, 250 parts of crystalline copper sulphate were introduced, and the pH was maintained at 5.5 by the addition of 40 parts of sodium carbonate. Then the mixture was heated at 65°C for 2 hours and suction-filtered while hot. The calcium sulphate which had been removed by filtration was washed with hot water. The combined filtrates were stirred at 40°C for 1 hour after the addition of a solution of 40 parts of sodium oxalate in 250 parts of water, and then clarified. By spray-drying of the dye solution thus obtained, 1090 parts of a salt-containing dye. In the form of the sodium salt, the dye was of the formula:



This dye dyed cotton fabrics to violet shades in the presence of alkaline agents; the dyeings obtained were fast to light and washing process.

Example 2.

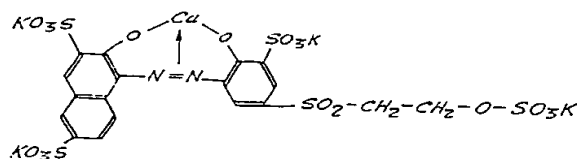
217 parts of 2-amino-4-(β-hydroxyethylsulphonyl)-phenol were esterified, sulphonated and diazotized in the same manner as described in Example 1. After the addition of a solution of 254 parts of 1-(4'-sulphophenyl)-3-methyl-pyrazolone-5 in 800 parts of water and 90 parts of 33% (by weight) sodium hydroxide solution, the pH-value was adjusted to 5 to 6.5 by alternating introduction of 700 parts of calcium carbonate and 2000 parts of ice, and, finally, 80 parts of sodium carbonate. At this pH, coupling was complete after a short time. By the addition of 250 parts of crystalline copper sulphate dissolved in 750 parts of water and 50 parts of sodium carbonate, the monoazo dye was converted at pH 5 into the copper complex monoazo dye. The reaction mixture containing calcium sulphate was stirred again at 65°C for 2 hours, and filtered while hot. The residue was washed with hot water. An aqueous solution of 40 parts of sodium oxalate was added to the combined filtrates, stirred at 40°C for 1 hour and, after clarification, evaporated to dryness *in vacuo* at 60°C. 984 parts of a salt-containing dye was obtained which, in the form of the sodium salt, was of the formula



This dye dyes cotton, according to the usual processes for dyeing and printing with reactive dyes, to intense, reddish-yellow shades; the prints have very good fastness properties to light and wet processing.

Example 3.

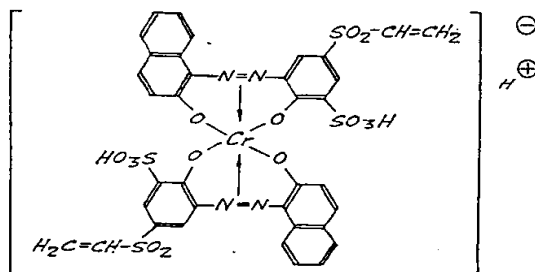
421 parts of the disodium salt of the 2-amino-4-(β-hydroxy-ethylsulphonyl)-phenol-6-sulphonic acid were dissolved in 450 parts by volume of 5 N hydrochloric acid, 500 parts of water and 500 parts of ice, and diazotized by introducing 200 parts by volume of 5 N sodium nitrite solution under the surface while stirring. After diazotisation had been completed, 3 parts of amidosulphonic acid were added. Then, a solution of 348 parts of the disodium salt of the 2-hydroxy-naphthalene-3,6-disulphonic acid were added in 800 parts of water. By introducing 180 parts of sodium bicarbonate, the pH was adjusted at 6. After coupling had been completed, 250 parts of crystallized copper sulphate were added, heated at 50°C while stirring, and the pH was maintained at 5 by the addition of 40 parts of sodium carbonate. The complex formation was complete after a short time. Then, 500 parts of potassium chloride were introduced and the solution was cooled while stirring. The salted dye which, is in the form of the potassium salt, was of the formula



was suction-filtered and dried. 960 parts of salt-containing dyestuff was obtained. This dye dyed cotton in processes commonly used for the dyeing of reactive dyes to intense bluish-red shades; the prints were distinguished by very good fastness properties as to light and wet processing.

Example 4.

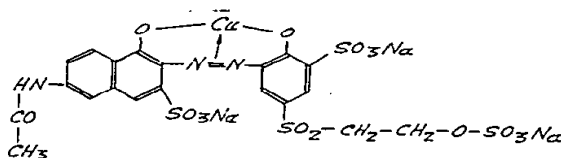
301 parts of the sodium salt of the 2-amino-4-vinylsulphonyl-phenol-6-sulphonic acid which were dissolved in a mixture of 450 parts by volume of 5 N hydrochloric acid, 500 parts of water and 500 parts of ice, were diazotized by the introduction of 200 parts by volume of 5 N sodium nitrite solution. After 15 to 30 minutes, 3 parts of amidosulphonic acid were added. While stirring and adding, alternately, 125 parts of sodium carbonate and a further 1000 parts of ice in portions, the solution was neutralized to a pH of 4 to 5. A solution of 144 parts of β -naphthol in 500 parts of water and 130 parts of a 33% sodium hydroxide solution were added. When coupling was complete (pH 7 to 8), 250 parts of chromic alum were introduced and the mixture was heated at 95° to 100°C. By the addition of 20 parts of sodium bicarbonate, the pH was maintained at 4.5 to 5. When the complex formation was complete, the pH was adjusted at 5.5 to 6 with 10 parts of sodium carbonate and the solution was spray-dried. 750 parts of a salt-containing dye was obtained, which in the form of the free acid, was of the formula



This dye dyed wool, according to usual dyeing processes, for example from a neutral dyebath, to reddish-grey shades, which showed very good fastness properties to light and washing processes.

Example 5.

217 parts of 2-amino-4-(β -hydroxyethylsulphonyl)-phenol were esterified, sulphonated and diazotized as described in Example 1. For coupling, 281 parts of 1-hydroxy-6-acetylamino-naphthalene-3-sulphonic acid were used instead of the 1-hydroxy-8-acetylamino-naphthalene-3,6-disulphonic acid. The reaction was continued in the same manner as described in Example 1. After isolating by spray-drying, 970 parts of a salt-containing dye were obtained. In the form of the sodium salt, this dye was of the formula



It dyes cotton fabrics, according to the processes commonly used in the dyeing and printing with reactive dyes, to intense bluish-red shades; these dyeings and prints were distinguished by very good fastness properties to light and wet processing.

It will be appreciated that the above dyes may be obtained in the free acid form or as a sodium or potassium salt irrespective of the form actually shown in the above formulae.

5 When proceeding in an analogous manner as described in the preceding Examples, and when converting the monoazo dyes obtained by coupling the diazo components enumerated in column 2 of the following Table with the coupling components enumerated in column 3 into the metal complex compounds by means of the metals indicated in column 4, metal complex monoazo dyestuffs are obtained which dye cotton or wool fibrous materials to the shades shown in column 5; the resulting dyeings and prints having good fastness properties similar to those described above. 10

TABLE

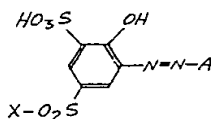
Example No.	Diazo component	Coupling component	Metal	Shade on Cotton
6	2-amino-4-(β -sulphatoethylsulphonyl)-phenol-6-sulphonic acid	1-hydroxy-8-amino-naphthalene-5,7-disulphonic acid	Cu	blue
7	"	"	Cr	blue
8	"	"	Co	reddish-violet
9	"	1-hydroxy-naphthalene-3-sulphonic acid	Cu	Bordeaux
10	"	"	Cr	violet
11	"	1-(4'-sulphophenyl)-3-carboxypyrazole-5	Cu	reddish-yellow
12	"	1-hydroxy-8-acetylamino-naphthalene-3,6-disulphonic acid	Cr	blue
13	2-amino-4-vinylsulphonyl-phenol-6-sulphonic acid	β -naphthol	Co	violet (on wool)
14	2-amino-4-(β -sulphatoethylsulphonyl)-phenol-6-sulphonic acid	1,3-diaminobenzene-4-sulphonic acid	Co	brown
15	"	1-hydroxy-7-acetylamino-naphthalene-3-sulphonic acid	Cu	Bordeaux
16	"	1-hydroxy-naphthalene-4-sulphonic acid	Cu	bluish-red
17	"	2-amino-naphthalene-6,8-disulphonic acid	Co	grey
18	"	1-hydroxy-6-acetylamino-naphthalene-3-sulphonic acid	Cr	violet
19	"	1-hydroxy-naphthalene-5-sulphonic acid	Cu	bluish-red

TABLE (Continued)

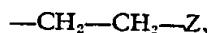
Example No.	Diazo component	Coupling component	Metal	Shade on Cotton
20	2-amino-4-(β -sulphatoethylsulphonyl)-phenol-6-sulphonic acid	2-hydroxy-naphthalene-6-sulphonic acid	Cu	bluish-red
21	"	2-amino-naphthalene-7-sulphonic acid	Co	grey
22	"	2-hydroxy-naphthalene-5-sulphonic acid	Cu	bluish-red
23	"	2-hydroxy-naphthalene-7-sulphonic acid	Cu	bluish-red
24	2-amino-4-(β -diethylaminoethylsulphonyl)-phenol-6-sulphonic acid	1-hydroxy-naphthalene-4-sulphonic acid	Cu	bluish-red
25	2-amino-4-(β -thiosulphatoethylsulphonyl)-phenol-6-sulphonic acid	"	Cu	bluish-red
26	2-amino-4-(β -phosphatoethylsulphonyl)-phenol-6-sulphonic acid	"	Cu	bluish-red
27	2-amino-4-(β -acetoxycethylsulphonyl)-phenol-6-sulphonic acid	"	Cu	bluish-red
28	2-amino-4-(β -chloroethylsulphonyl)-phenol-6-sulphonic acid	"	Cu	bluish-red
29	2-amino-4-(β -phenoxyethylsulphonyl)-phenol-6-sulphonic acid	"	Cu	bluish-red
30	2-amino-4-(β -sulphatoethylsulphonyl)-phenol-6-sulphonic acid	1-acetoacetyl-amino-benzene-4-sulphonic acid	Cu	yellow
31	"	1,3-dihydroxybenzene	Co	brown
32	"	1,3-dihydroxy-4-methylbenzene	Cr	brown

WHAT WE CLAIM IS:—

1. A water-soluble metal complex compound of a monoazo dye which dye, in the non-metallized free acid form, is of the general formula



5 in which formula X represents a vinyl group or a group of the formula



Z representing a hydroxy group or an inorganic radical that can be split off by an alkaline agent; and A represents a radical of a coupling component of the phenol, aniline, naphthol, or naphthylamine series, the hydroxy or amino group of which is *ortho* to the azo group, a radical of a coupling component of the 5-(hydroxy or amino)-pyrazole series, additionally substituted in the 1- and 3-positions, or a radical of a coupling component of the acetoacetic acid arylamide series, the metal forming the complex being copper, chromium or cobalt, and any sulphonic acid group in the compound being in the free acid form or in the form of a sulphonate group.

2. A compound as claimed in claim 1, wherein Z represents a halogen atom, an alkylsulphonic acid ester group, an arylsulphonic acid ester group, a carboxylic acid acyloxy group, or a dialkylamino group.

3. A compound as claimed in claim 1, wherein Z represents a chlorine atom, a bromine atom, a methylsulphonyloxy group, a *p*-toluenesulphonyloxy group, an acetoxy group, a 3-sulphobenzoyloxy group, a phenoxy group, a dimethylamino group, a diethylamino group, a thiosulphuric acid ester group or a phosphoric acid ester group.

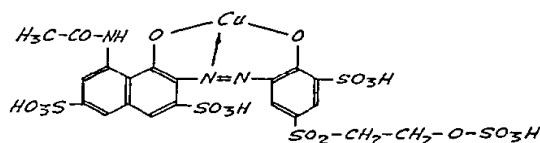
4. A compound as claimed in claim 1, wherein Z represents a sulphuric acid ester group.

5. A compound as claimed in any one of claims 1 to 4, wherein the metal forming the complex is copper.

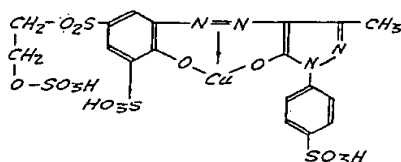
6. A compound as claimed in claim 1, wherein the metal forming the complex is copper and X represents a β -sulphatoethyl group.

7. A compound as claimed in any one of claims 1 to 6, wherein the group A is derivable from any one of the compounds of general formula (3) specifically listed herein by removal of a hydrogen atom from said compound.

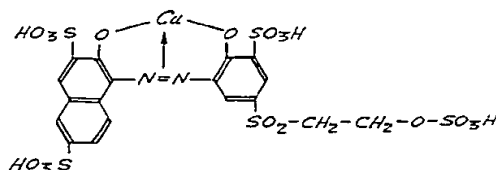
8. The compound of the formula



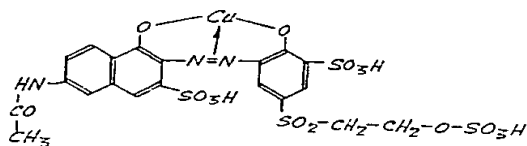
9. The compound of the formula



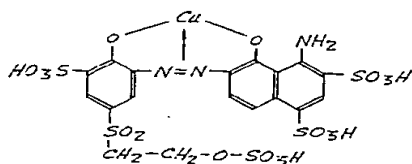
10. The compound of the formula



11. The compound of the formula



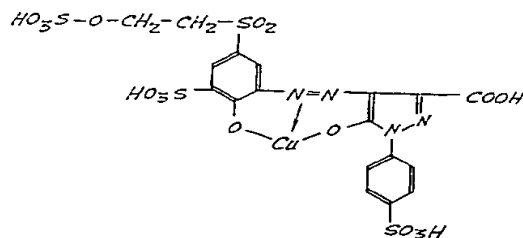
12. The compound of the formula



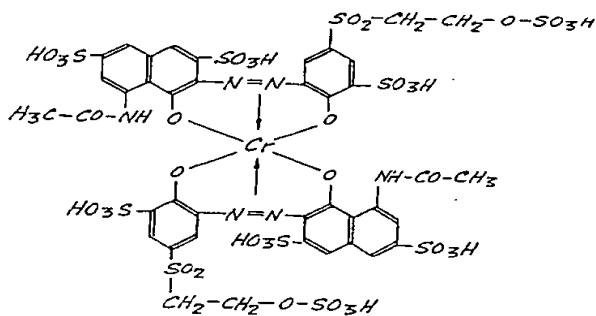
5

13. The compound of the formula

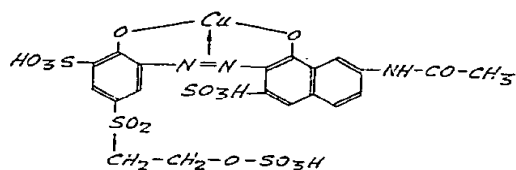
5



14. The compound of the formula



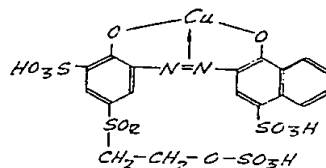
15. The compound of the formula



10

10

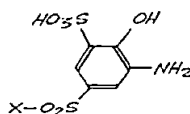
16. The compound of the formula



17. A compound as claimed in any one of claims 8 to 16, in the form of its sodium or potassium salt.

18. A compound as claimed in claim 1 and described in any one of Examples 4, 7 to 10, 13, 14 and 17 to 32.

19. A process for the manufacture of a compound as claimed in claim 1, which process comprises diazotizing an amine of the general formula



in which X is defined as in claim 1, coupling it with a coupling component of the general formula



in which A is defined as in claim 1, and treating the mono-azo dyestuff thus obtained with a copper-, chromium- or cobalt-yielding agent.

20. A process as claimed in claim 19, wherein the coupling component is a naphthalene sulphonic acid.

21. A process as claimed in claim 19, wherein the coupling component is any one of those specifically mentioned herein.

22. A process as claimed in claim 19 conducted substantially as described herein.

23. A process as claimed in claim 19 conducted substantially as described in any one of the Examples herein.

24. A compound as claimed in claim 1 whenever prepared by a process as claimed in any one of claims 19 to 23.

25. A dyeing or printing process wherein a dyestuff as claimed in any one of claims 1 to 18 and 24 is used.

26. Leather or a fibrous material comprising wool, silk, a synthetic polyamide and/or natural or regenerated cellulose, which has been dyed or printed with a dye claimed in any one of claims 1 to 18 and 24.

ABEL & IMRAY,
Chartered Patent Agents,
Northumberland House,
303-306 High Holborn,
London, WC1V 7LH.

Reference has been directed in pursuance of Section 9, Subsection (1) of the Patents Act 1949, to Patents Nos: 1,075,074; 913,517 and 913,511.

THIS PAGE BLANK (USPTO)